INTERACTION OF A GLASS SUBSTRATE WITH SOL-GEL SOLUTIONS

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The possible stages of interaction between glass and film-forming solutions are considered. The effect of the amounts of acid and water in solution of the destruction of glass is demonstrated. An analysis of the relationship between the quantities of Na_2O and SiO_2 and the transition-layer width is provided.

The effect of the composition of sol-gel films on the diffusion of sodium, calcium, and silicon ions from the glass substrate into the film was considered in [1]. The results of the study indicated that the intensity of migration of the specified components from glass is closely related to the amount of hydrochloric acid in the film-forming solution (FFS), on the one hand, and on the film structure specifics, on the other hand.

The purpose of the present paper is to clarify the mechanism of the reaction of the FFS with the glass substrate. The compositions under consideration and the methods for preparing solutions, deposition, firing, and testing of films were considered earlier [1].

Table 1 shows the molar content of oxides (based on synthesis) in film coatings, the amount of hydrochloric acid (converted to 100 wt.%) per 100 g of solution, the amount of water introduced into the system with the concentrated hy-

drochloric acid, ethanol, and crystal hydrates of the initial salts, as well as the weight of non-fixed HCl (a value numerically equal to the difference between the total HCl content in the solution and its quantity needed for the transformation of the film-forming oxides into the respective chlorides).

A film-forming solution is a complex aggressive medium. Entering in contact with the solution, the glass substrate is subjected to the effect of hydrochloric acid, water, ethanol, chlorides of the film-forming elements, and the products of reactions between all the listed components. The present study analyzes the effect of water and acid, which are the most reactive components of the FFS, on the substrate.

Table 1 indicates that the quantity of Na_2O and SiO_2 in the considered films ranges from 2 to 37 and from 0 to 79%, respectively, whereas the width of the glass – film transition layer varies from 1200 to 8400 Å. It can be seen in Fig. 1 that the contents of sodium and silicon oxides in the films are related by a dependence which is close to an inverse one. In

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TABLE 1

Film composition,* mol.%	Content per 100 g of FFS, g			Diffused into film, mol.%		Transition-layer width, Å
	HCl_{tot}	$HCl_{non\text{-}fixed}$	H_2O	Na_2O	SiO_2	
80% Sb_2O_3, 20% ZrO_2	16.9	7.2	15.2	16	27	3090 – 3210
80% Sb_2O_3, 20% SiO_2	17.9	10.2	15.7	10	13	8060 – 8160
80% Sb_2O_3, 20% Bi_2O_3	17.1	7.5	15.2	6	79	3300 – 3380
80% Sb_2O_3, 20% In_2O_3	19.7	8.8	16.9	37	0	8700 – 9490
80% Sb_2O_3, 20% La_2O_3	17.2	6.8	15.4	36	0	8260 – 8440
80% In_2O_3, 20% ZrO_2	21.1	11.0	17.8	2	77	1230 – 1370
80% In_2O_3, 20% SiO_2	22.3	10.7	18.5	16	42	3700 – 3800
80% In_2O_3, 20% La_2O_3	21.0	9.9	17.6	5	59	3500 – 3700
80% In_2O_3, 20% TiO_2	22.1	10.5	18.5	28	0	4980 – 5080
80% La_2O_3, 20% SiO_2	11.2	9.2	11.7	15	10	5180 – 5300
80% La_2O_3, 20% Bi_2O_3	12.1	3.2	15.3	12	20	5380 – 5560
80% La_2O_3, 20% Sb_2O_3	13.0	3.2	11.1	11	58	4100 – 4200
80% ZrO_2, 20% La_2O_3	4.7	0.9	7.6	3	41	3050 – 3150
80% TiO_2, 20% La_2O_3	7.2	4.9	10.4	14	0	7000 – 7740

* All films contain Fe_2O_3.
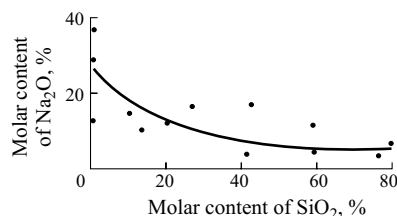
Fig. 1. Dependence of Na_2O content in the film on the amount of SiO_2.
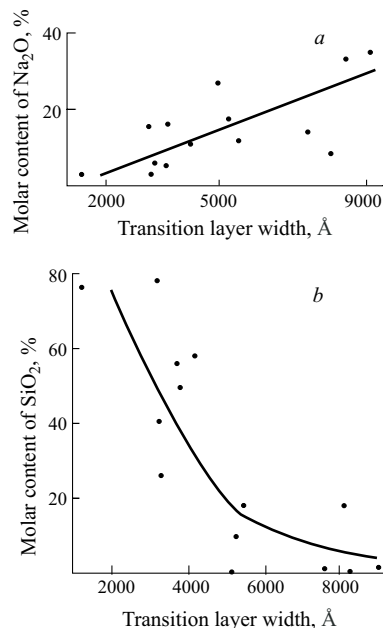

Fig. 2. Dependence of Na_2O (*a*) and SiO_2 (*b*) content in the film on the width of the transition layer.

other words, the specified components are antagonists and can be said to oppose the penetration of each other.

The Na_2O quantity is proportional to the transition-layer width, and SiO_2 is inversely proportional to that parameter (Fig. 2).

In order to interpret these results, let us consider the possible stages of reactions of the FFS components with glass. Apparently, at the first stage, the acid facilitates leaching of sodium ions, and they accumulate in the solution layer adjacent to the glass, which subsequently serves to form the thin film. By analogy with the term proposed by A. A. Appen [2], let us call this stage "the acid attack." Its intensity is directly related to the quantity of acid in the solution, the result of which is a high concentration of Na_2O in the coating. The data in Table 1 substantiate this assumption. In theory, the curve of sodium distribution in the glass – solution system most probably should be similar to the curve shown in Fig. 3*a* [3, 4].

In the opinion of Bezborodov [5], the silicon-oxygen skeleton is not destroyed by hydrochloric acid. However, the

concentration of SiO_2 in the layer of glass modified by the acid attack should increase toward the surface due to washing out of sodium ions. If SiO_2 does not make up part of the FFS, its theoretical distribution in the FFS – glass system should be similar to the one shown in Fig. 3*b* [3, 4]. As a consequence of the mutual penetration of glass components into the solution and vice versa, the curves indicated in Fig. 3*a* and *b* will presumably be smoothed in the way shown in Fig. 3*c* [3]. In fact, the majority of distribution curves for sodium and silicon in the considered systems are close to the curves shown in Fig. 3*c*.

The sodium ions accumulated in the solution layer adjacent to the glass enter in a reaction with impurity water. As the result, sodium hydroxide is formed, which is responsible for the alkaline attack that may evolve at the second stage of the interaction between the glass and the FFS. The alkali dissolves the silicon-oxygen skeleton. The silicon ions penetrate into the solution and intensely enrich its layer adjacent to the glass. Thus, the thickness of the layer leached at the first stage should regularly decrease. On the whole, the film will become richer in silicon and poorer in sodium. This is supported by the experimental data in Table 1 and in Fig. 1. It can be expected that the content of silicon in the film, which is determined by the intensity of the alkaline attack, is inversely proportional to the size of the glass – film transition layer (Fig. 2*b* and Table 1).

On the contrary, the acid attack, whose intensity is determined by the quantity of sodium oxide contained in the film, should lead to enlarging of the transition-layer width (Fig. 2*a* and Table 1).

Let us discuss the factors determining the probability of the emergence and the intensity of acid and alkaline attacks in the interaction between the FFS and the glass substrate.

Let us consider two films: 80% Sb_2O_3, 20% Bi_2O_3, Fe_2O_3 and 80% Sb_2O_3, 20% La_2O_3, Fe_2O_3. It can be seen from Table 1 that the content of HCl in both solutions is virtually identical. However, the weight of non-fixed hydrochloric acid in the first FFS is 0.7 g greater than in the second solution. Consequently, the intensity of the acid attack evolving during the reaction of the first solution with glass is higher. This means that at this particular stage, a higher amount of sodium oxide is leached from the glass substrate treated by the first FFS and is dissolved in a smaller amount of water (the H_2O content in the first and in the second FFS is equal to 15.2 and 15.4 g, respectively) and, accordingly, a more concentrated alkali solution is formed. As the result, an intense alkaline attack will evolve in the interaction of the first FFS and the substrate, as a consequence of which the Na_2O content in the film will drop to one-sixth, the Si_2O concentration will significantly increase, and the width of the transition layer will become 2.5 times smaller.

The same regularity can be observed in comparing the following pairs of films (Table 1): 80% In_2O_3, 20% SiO_2, Fe_2O_3 and 80% In_2O_3, 20% TiO_2, Fe_2O_3; 80% Sb_2O_3, 20% Bi_2O_3, Fe_2O_3 and 80% Sb_2O_3, 20% ZrO_2, Fe_2O_3; 80% In_2O_3,
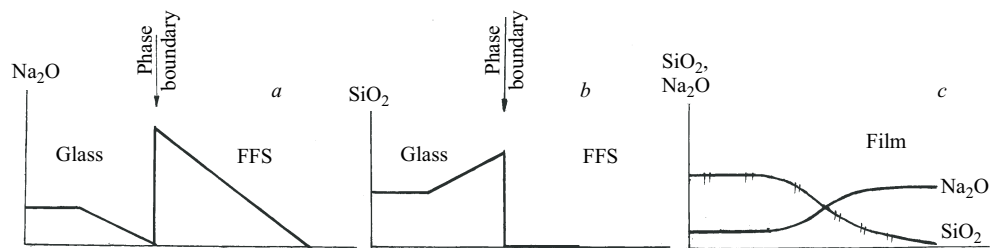
Fig. 3. Distribution of Na_2O (a) and SiO_2 (b) in the glass – FFS system; distribution of Na_2O and SiO_2 in the glass – film system (c).

20% ZrO_2, Fe_2O_3 and 80% In_2O_3, 20% La_2O_3, Fe_2O_3; 80% La_2O_3, 20% Bi_2O_3, Fe_2O_3 and 80% La_2O_3, 20% Sb_2O_3, Fe_2O_3.

Thus, the intensity of the acid attack depends on the amount of acid, and the intensity of the alkaline attack depends on the concentration of water in the FFS.

The interaction of glass with the solution in sol-gel technology proceeds in two stages. At the first stage, under the effect of acid, sodium oxide is leached from the glass and dissolved in water. At the second stage, the resulting alkali destroys the silicon-oxygen skeleton of the substrate.

The contents of Na_2O and SiO_2 in the considered sol-gel films are related by inversely proportional dependences. The thickness of the glass – film transition layer increases in proportion to the increasing Na_2O content and decreasing quantity of SiO_2 in the coating.

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